

The University of Chicago

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 $\text{CaSiO}_3\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-NaAlSiO}_4$

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY AND PALEONTOLOGY

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W. K. GUMMER

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ABSTRACT

Phase equilibria at high temperatures have been investigated experimentally in the system CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - NaAlSiO_4 . The results, presented in tables and equilibrium diagrams, enable a discussion of courses of crystallization in typical mixtures of these compounds and throw some light on the development and interrelations of the minerals nepheline, plagioclase, melilite, and wollastonite in rocks.

INTRODUCTION

This investigation deals with the phase equilibria, at high temperatures but at normal pressures, of the following three rock-forming silicates: calcium metasilicate CaSiO_3 , calcium-aluminum silicate $\text{CaAl}_2\text{Si}_2\text{O}_8$, and sodium-aluminum orthosilicate NaAlSiO_4 . These compounds do not occur pure in nature; nevertheless, they are dominant in the rock-forming minerals wollastonite, anorthite, and nepheline, respectively. The melting and inversion phenomena of the individual silicates were not studied by the writer, since these data are available from previous studies. For the same reason the three binary systems that can be formed of these three components were not investigated except in special compositions, to be discussed.

The minerals studied are of fairly widespread occurrence in nature. Wollastonite has perhaps the least extensive provenance, having been recognized chiefly in rocks that have undergone metamorphism; but it has been reported

from several localities as being a primary mineral resulting from the crystallization of magmas.¹ It is especially associated with nepheline in some varieties of the alkaline suite of rocks. Pseudowollastonite is reported only once.² Anorthite, as a constituent of the plagioclase feldspars, is of prime importance in rocks. Plagioclase occurs with most minerals, including wollastonite and nepheline. Nepheline is a characteristic mineral of the alkaline rocks, both felsic and basic.³ Recent work has shown some nepheline

¹ E. S. Bastin and J. M. Hill, "The Evergreen Copper Mine, Colorado," *Econ. Geol.*, Vol. VI (1911), pp. 465-72; C. E. Tilley and H. F. Harwood, "The Dolerite-Chalk Contact of Scawt Hill, County Antrim: The Production of Basic Alkaline Rocks, etc.," *Min. Mag.*, Vol. XXII (1931), pp. 440-68; P. G. Sohngé, "Paragenesis of the Khan Pegmatite, South West Africa," *Trans. Geol. Soc. South Africa*, Vol. XLII (1939), pp. 23-34.

² W. F. P. McLintock, "On the Metamorphism Produced by Combustion of Hydrocarbons in the Tertiary Sediments of South West Persia," *Min. Mag.*, Vol. XXIII (1932), pp. 207-28.

³ F. D. Adams and A. E. Barlow, "Geology of the Haliburton and Bancroft Areas, Province of Ontario," *Can. Dept. of Mines, Geol. Surv. Branch, Mem. No. 6* (1910).

rocks to have formed, through a process analogous to granitization, from impure limey sediments.⁴

The presence of free alumina in the system is of interest since corundum is another typical mineral—albeit in most

again, this group is characteristic of the alkaline rocks. Therefore, this study may be of importance in connection with questions of the origin of alkaline rocks.

All mixtures of the three compounds lie within the four-component system

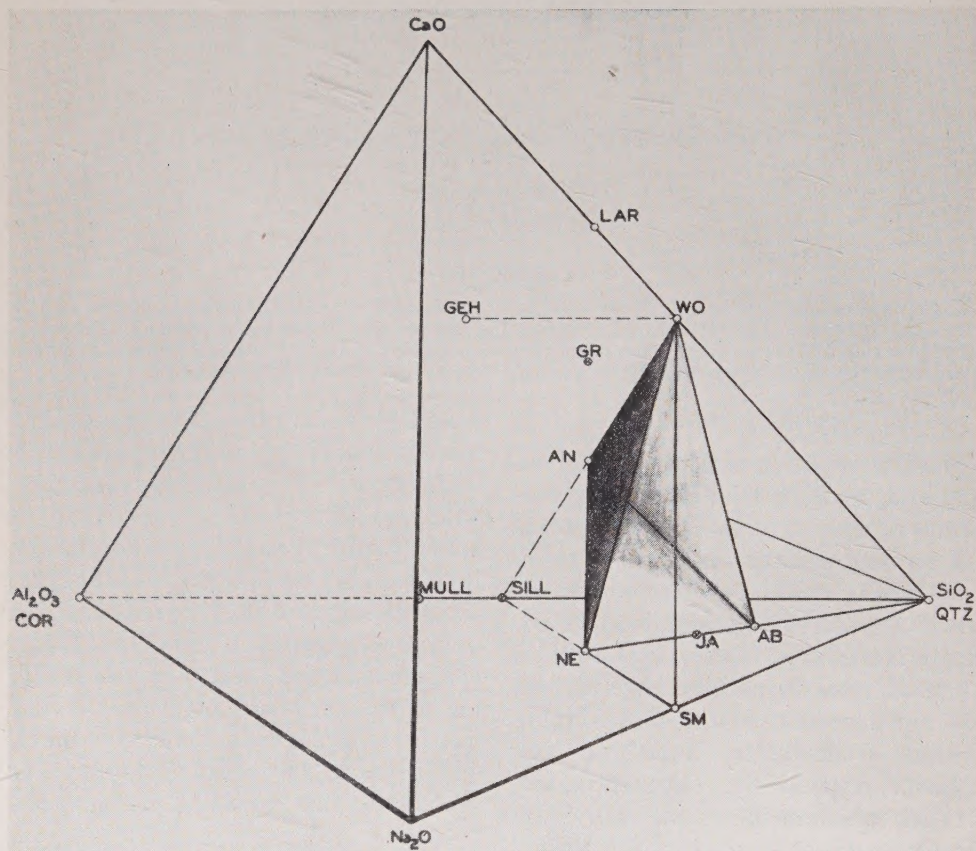


FIG. 1.—The soda-lime-alumina-silica tetrahedron. Showing the location of the system wollastonite-anorthite-nepheline. Compounds formed artificially are shown thus: $\otimes$; those occurring naturally, $\circ$. The abbreviations signify: AB, albite; AN, anorthite; COR, corundum; GEH, gehlenite; GR, grossularite; JA, jadeite; LAR, larnite; MULL, mullite; NE, nepheline; QTZ, quartz; SILL, sillimanite; SM, sodium metasilicate; and WO, wollastonite.

cases accessory—of the syenitic alkaline rocks.

A mineral of the melilite group has been encountered in the melts, and,

$\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, which is presented in Figure 1 as the conventional tetrahedron. The plane of the system $\text{CaSiO}_3-\text{CaAl}_2\text{Si}_2\text{O}_8-\text{NaAlSiO}_4$ cuts across the interior of the tetrahedron.

Sixty mixtures of the three compounds in various proportions have been

⁴ W. K. Gummer and S. V. Burr, "The Nephelized Paragneisses of the Bancroft Region, Ontario" (abstr.), *Science*, Vol. XCVII (1943), p. 286.

studied as to thermal behavior. The quenching method was utilized, whereby a small charge of a mixture is held at a constant temperature for a time sufficient to insure the establishment of equilibrium. Instantaneous cooling is provided by dropping the charge into mercury, thus permitting microscopic examination of the phases that were present during the run. Approximately 260 individual runs were carried out.

PROPERTIES OF THE COMPOUNDS

CaSiO_3

CaSiO_3 has three modifications, of which pseudowollastonite, melting at $1,544^\circ\text{C}$,⁵ and wollastonite, inverting to pseudowollastonite at about $1,125^\circ\text{C}$,⁶ are the most important ones. Only pseudowollastonite was met with at liquidus temperatures in this study. This phase occurs typically in rather equant grains of near-hexagonal cross section and with sensibly parallel extinction in prismatic sections. Elongation is generally negative. The crystal symmetry is probably monoclinic, with $a = 1.610$, $\beta = 1.611$, and $\gamma = 1.654$. Polysynthetic twinning occurs in some cases.

$\text{CaAl}_2\text{Si}_2\text{O}_8$

Pure $\text{CaAl}_2\text{Si}_2\text{O}_8$ has only one modification, anorthite, which melts at $1,552^\circ\text{C}$. It is triclinic, with $a = 1.5755$, $\beta = 1.5832$, and $\gamma = 1.5885$. Crystals obtained in quenches are commonly platy, b(010) showing the greatest development; and they appear four- or six-sided or lathlike. Laths are commonly warped and twinned after the Albite Law.

⁵ E. F. Osborn and J. F. Schairer, "The Ternary System, Pseudowollastonite-Akermanite-Gehlenite," *Amer. Jour. Sci.*, Vol. CCXXXIX (1941), p. 719.

⁶ *Ibid.*, p. 721.

NaAlSiO_4

NaAlSiO_4 has at least four modifications. Carnegieite melts at $1,526^\circ\text{C}$,⁷ is isometric at the temperature of formation, and inverts at 690°C . to a triclinic(?) form.⁸ The indices of the low-temperature form are given by Bowen⁹ as $\omega = 1.509$, $\epsilon = 1.514$; crystal form is generally lacking, but isometric characteristics have been observed. It is commonly globular and intricately twinned.

Nepheline inverts to carnegieite at $1,254^\circ \pm 5^\circ\text{C}$.¹⁰ It is hexagonal and is obtained commonly with prisms and basal pinacoid. Rather rarely it occurs in clusters of fine needles. Bowen gives the indices as $\omega = 1.537$, $\epsilon = 1.533$. The indices of the limiting solid solution of anorthite in nepheline, $\text{Ne}_{65}\text{An}_{35}$, are $\omega = 1.537$, $\epsilon = 1.539$. The sign of the nephelines obtained at liquidus temperatures in various mixtures has been plotted on the composition triangle, Figure 16.

$\text{Ca}_2\text{Al}_2\text{SiO}_7$

The possible extent of solid solution in the phase termed "gehlenite" is not known. Gehlenite proper is tetragonal, with $\omega = 1.669$ and $\epsilon = 1.658$, and melts at $1,590^\circ \pm 2^\circ\text{C}$.¹¹ The crystals found in quench products are parallelopipeds with high indices, low birefringence, and positive elongation. They are usually blocky, with rather indefinite elongation, though

⁷ N. L. Bowen, "The Binary System NaAlSiO_4 (Carnegieite, Nepheline)— $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Anorthite)," *Amer. Jour. Sci.*, Vol. XXXIII (4th ser., 1912), pp. 551-73.

⁸ N. L. Bowen and J. W. Greig, "The Crystalline Modifications of NaAlSiO_4 ," *Amer. Jour. Sci.*, Vol. X (5th ser., 1925), pp. 204-12.

⁹ Bowen, ftn. 7 (1912).

¹⁰ J. W. Greig and Tom F. W. Barth, "The System $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (Nephelinite, Carnegieite)— $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (Albite)," *Amer. Jour. Sci.*, Vol. XXXV-A (5th ser., 1938), pp. 94-112.

¹¹ Osborn and Schairer, ftn. 5 (1941).

they may be tabular parallel to the base. Rarely, eight-sided crystals were obtained; this habit, two prisms and base, is characteristic of the melilite group. Still more rarely sections were found that showed the presence of three-prism forms.

Beta- Al_2O_3

The β -alumina encountered has high relief, high birefringence, parallel extinction, and positive elongation. G. A. Rankin and H. E. Merwin¹² gave the values $\omega = 1.677 \pm 0.003$ and $\epsilon = 1.635 - 1.650$ for the phase found in preparations of "pure" Al_2O_3 . β - Al_2O_3 occurs typically as thin hexagonal plates, but perfect form is not always developed. In subliquidus runs very well-formed crystals were found. Commonly a number of hexagonal plates are in parallel orientation and optic continuity.

Rankin and Merwin suggested that β - Al_2O_3 melts at $2,050^\circ \pm 20^\circ \text{C}$. The exact relations between α - Al_2O_3 and β - Al_2O_3 are not thoroughly understood; β - Al_2O_3 is apparently monotropic with respect to α - Al_2O_3 . A considerable literature has arisen as a result of chemical and X-ray investigation of the β -form, and the most recent work suggests that it has actually the composition $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$,¹³ analogous to another artificial compound, $\text{K}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$.

THERMAL DATA

THE BINARY SYSTEM CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$

The system CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ was first approximated in the work of Rankin and Wright¹⁴ on the system CaO - Al_2O_3 -

¹² "The Ternary System, CaO - Al_2O_3 - MgO ," *Jour. Amer. Chem. Soc.*, Vol. XXXVIII (1916), pp. 568-88.

¹³ C. A. Beevers and M. A. S. Ross, "The Crystal Structure of 'Beta Alumina,'" *Zeitschr. f. Kryst. u. Min.*, Vol. XCVII (1937), pp. 59-66.

¹⁴ G. A. Rankin and F. E. Wright, "The Ternary System, CaO - Al_2O_3 - SiO_2 ," *Amer. Jour. Sci.*, Vol. XXXIX (4th ser., 1915), pp. 1-79.

SiO_2 . Recently Osborn has made a more detailed study of the thermal relations between the two compounds and places the eutectic at $1,307^\circ \text{C}$. Two Japanese students¹⁵ placed the eutectic between pseudowollastonite and anorthite at $1,283^\circ \text{C}$. Osborn's results (Fig. 2) have been accepted by the writer as more accurate and in agreement with the present results.

THE BINARY SYSTEM CaSiO_3 - NaAlSiO_4

The system CaSiO_3 - NaAlSiO_4 was investigated by W. R. Foster,¹⁶ the results of whose studies are shown in Figure 3. The melting-point of pseudowollastonite was taken from the work of Osborn and Schairer¹⁷ as $1,544^\circ \text{C}$., and the melting-point of carnegieite from the work of Bowen¹⁸ as $1,526^\circ \text{C}$. The eutectic composition as determined by Foster is about 58 per cent nepheline at a temperature of $1,164^\circ \text{C}$. However, he himself states that some glass was still present a few degrees below this temperature. The writer made determinations on three mixtures of this system and found that glass first formed from devitrified mixtures at a temperature of $1,155^\circ \pm 2^\circ \text{C}$. Small amounts of glass could well escape notice; therefore the temperature may be still lower.

The break on the liquidus caused by the inversion of nepheline to carnegieite occurs at $1,267^\circ \text{C}$., 13° higher than the figure for the pure compound. That rise is due to solid solution in the nepheline, or, if in both nepheline and carnegieite, then to a greater extent in the nepheline. Foster suggests that between 5 and 10

¹⁵ K. Iwase and U. Nisioka, "The System CaTiSiO_5 - CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$," quoted in *Jour. Cer. Soc.*, Vol. XXI (1938), Suppl., p. 145.

¹⁶ "The System $\text{NaAlSi}_3\text{O}_8$ - CaSiO_3 - NaAlSiO_4 ," *Jour. Geol.*, Vol. L (1942), pp. 152-73.

¹⁷ Osborn and Schairer, ftn. 5 (1941).

¹⁸ Bowen, ftn. 7 (1912).

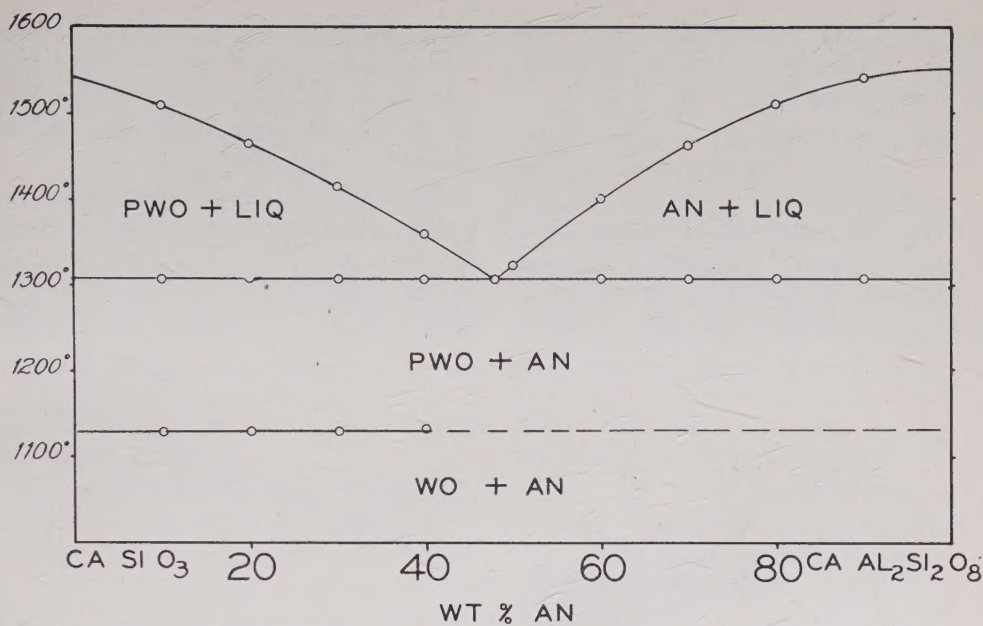


FIG. 2.—Phase relations in the binary system CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ (after Osborn and Schairer)

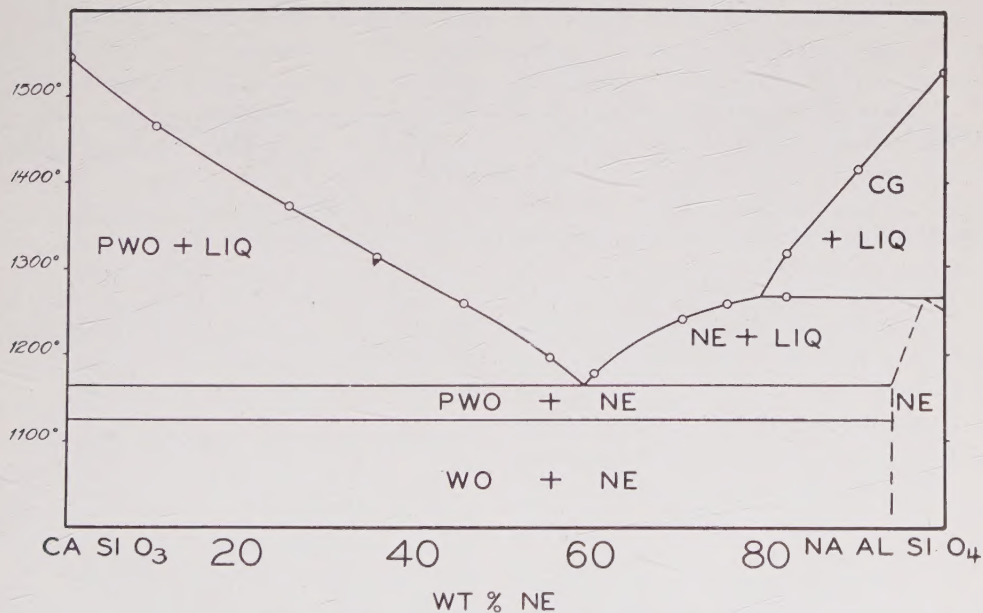
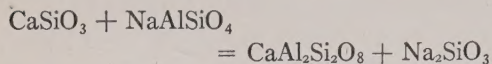


FIG. 3.—Phase relations in the system CaSiO_3 - NaAlSiO_4 (after Foster)

per cent CaSiO_3 may be taken into solid solution by nepheline. From a consideration of the reaction



it seems likely that the substance that is responsible for the rise of the inversion temperature is $\text{CaAl}_2\text{Si}_2\text{O}_8$. The ability of nepheline to hold considerable anorthite

parture from binary behavior, although perhaps not of great degree. The liquid would leave the system as a result of this effect and at once enter the system $\text{Na}_2\text{SiO}_3\text{--CaSiO}_3\text{--NaAlSiO}_4$.

The inversion of pseudowollastonite to wollastonite occurs at a subliquidus temperature, placed by Foster at $1,124^\circ\text{C}$. on the basis of results obtained in the system $\text{NaAlSi}_3\text{O}_8\text{--CaSiO}_3$. An attempt

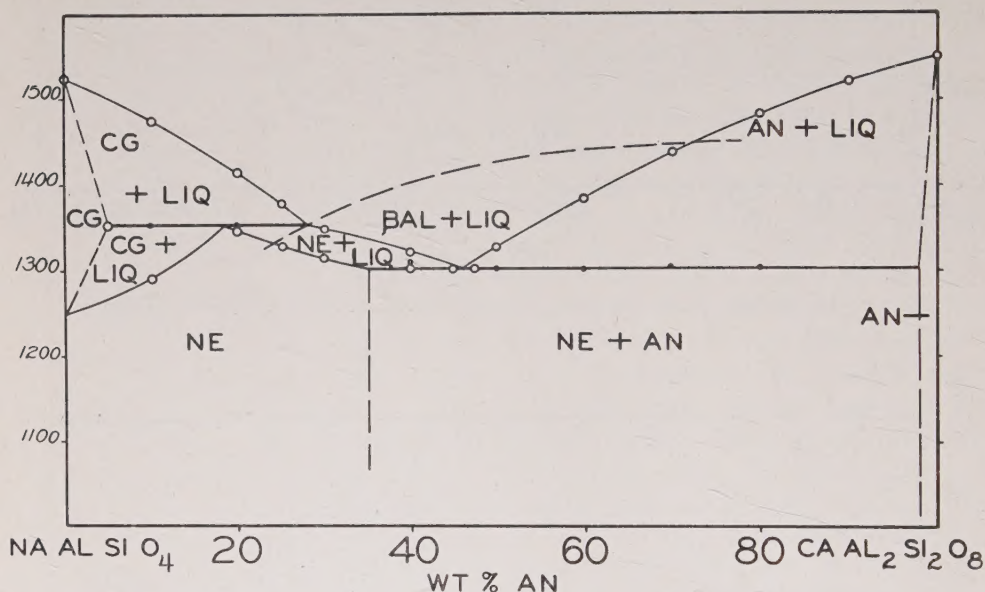


FIG. 4.—Phase relations in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ (after Bowen), with modifications after Schairer and the writer. The solid dots represent heating-curve breaks; the circles, quenching results.

in solid solution is known. The result of this reaction is to liberate sodium metasilicate, which will accumulate in the rest-liquid, since it does not enter into nepheline in solid solution.¹⁹ It does, however, form solid solutions with carnegieite, and this introduces a peculiar complication requiring further discussion later.

If anorthite separates in a nepheline solid solution, there is necessarily a de-

by Foster to obtain a compound such as the one-to-one molar compound between wollastonite and nepheline, which would be of melilite type, was unsuccessful.

THE BINARY SYSTEM $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$

The system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ has been investigated by Bowen,²⁰ and his results are presented in Figure 4, somewhat modified by a recent addition. This system exhibits the phenomenon of partial solid solution between the two end-members, which, coupled with the in-

¹⁹ C. E. Tilley, "The Ternary System, $\text{Na}_2\text{SiO}_3\text{--Na}_2\text{SiO}_5\text{--NaAlSiO}_4$," *Min. u. petrog. Mitt.*, Vol. XLIII (1933), pp. 406-21.

²⁰ Bowen, *ftn. 7* (1912).

version of carnegieite to nepheline, introduces complexity. Bowen placed the eutectic at 46 per cent anorthite and $1,304^\circ\text{C}$. There is a sharp break between the liquidi of nepheline and carnegieite, owing to inversion. Bowen placed the inversion at $1,352^\circ\text{C}$., a rise of 104°C . over the inversion in the pure substance. This rise is the result of the solid solution of anorthite in nepheline, up to 35 per cent by weight. The extent to which solid solution occurs in carnegieite is small—not more than 5 per cent, and possibly much less.

Recently Schairer²¹ has investigated the system $\text{NaAlSiO}_4\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--SiO}_2$, and in mixtures adjacent to the binary between nepheline and anorthite he met with a crystalline phase that he identified as β -alumina. He prepared mixtures along that join and obtained free alumina in them also. Bowen had found "alumina"—the β -form was not at that time recognized—in some of his mixtures but had attempted to account for it by loss of soda through volatilization at the high temperatures required for fusion of the preparations. It now seems certain that a field of alumina is present in the center of the binary, although the exact configuration of the liquidus is not known. This, of necessity, upsets the binary relations of the system. The field of β -alumina bridges the fields of anorthite and nepheline and possibly also reaches into the field of carnegieite, although the results of the writer do not so indicate. The field of β -alumina is a section of the field of alumina in the parent-tetrahedron.

The writer determined some of the thermal relations in one preparation, $\text{Ne}_{70}\text{An}_{30}$; at the liquidus temperature, $1,347^\circ\text{C}$., β -alumina is present, but it disappears simultaneously with the neph-

eline solid solution at approximately the temperature at which the nepheline inverts to carnegieite. This is not in agreement with the results of Schairer, who places the alumina liquidus for the mixture $\text{Ne}_{72}\text{An}_{28}$ some 50° higher. At lower temperatures, down to $1,316^\circ\text{C}$., the alumina seems to increase in quantity; and at that temperature there is still some glass present, although, according to Bowen's diagram, the solidus of the nepheline solid solutions is at approximately $1,315^\circ\text{C}$. The liquidus for β -alumina has been added to Bowen's diagram, based on results obtained both by Schairer and the writer (dashed line, Fig. 6). It must be stressed that this curve is based on very scanty data and does not agree in entirety with Schairer's determinations.

It should be noted that the field of nepheline plus liquid, as outlined by Bowen, has become a field of nepheline, β -alumina, and liquid; similarly, other fields in which β -alumina appears are now ternary. The delineation of the field of β -alumina, subliquidus, has not been completed, but that phase is present in several mixtures at temperatures around $1,200^\circ\text{C}$. Bowen has indicated that on cooling there is no change in the amount of anorthite soluble in nepheline. However, a very small amount of anorthite was observed in the mixture $\text{Ne}_{70}\text{An}_{30}$, at a temperature of $1,205^\circ\text{C}$., along with nepheline solid solution and β -alumina. This is far from proof that the amount of anorthite in solid solution decreases so rapidly at lower temperatures, especially since the original material contains nepheline, β -alumina, and very rare anorthite. Possibly, longer runs would have caused the removal of the anorthite from the devitrified mixture. Unfortunately, the temperature at which the mixture was originally devitrified is not known.

²¹ Unpublished data.

THE SYSTEM $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$

The investigation of the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ has yielded some interesting data. Fifty-four mixtures were investigated as to their thermal behavior, and the more important data are presented in Table I. The phase

nary system soda-lime-alumina-silica. Therefore, liquids in, or reaching, these areas behave in quaternary fashion. And, although there has been no manner of determining the exact nature of the nepheline solid solutions, these actually may be ternary solid solutions of such com-

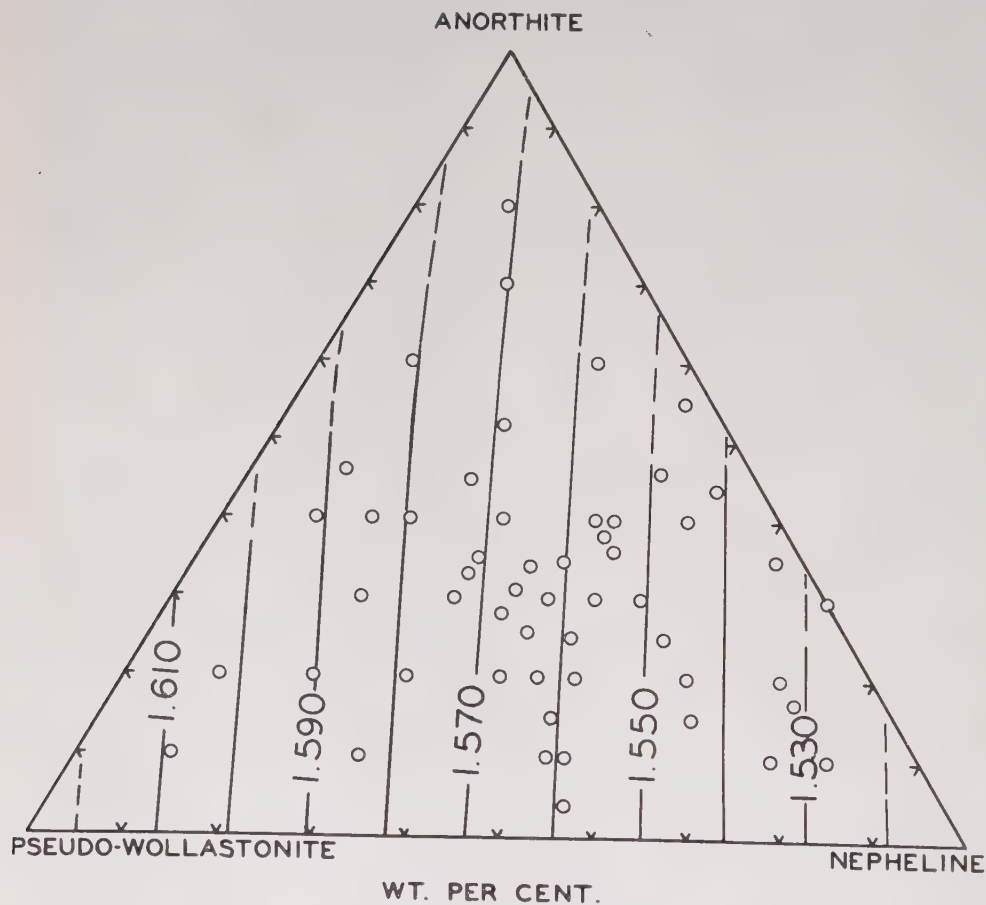


FIG. 5.—Isofract chart for glasses in the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$

relations are shown in Figures 6 and 7. The isofract chart is given as Figure 5.

Since two of the limiting systems, $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ and $\text{CaSiO}_3\text{--NaAlSiO}_4$, are not binary throughout, the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ is not ternary throughout. Two fields encroach on the system, from the quater-

position that behavior in the field of nepheline is also quaternary. Also, the plagioclase separating will be not pure anorthite but a basic plagioclase, since the formation of free alumina results in the production of albite. There is, therefore, a great deal of complication in this system; exact courses of crystallization

TABLE 1

THERMAL DATA FOR THE SYSTEM $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$

WEIGHT PER CENT			TIME	TEMP. (CENTIGRADE)	FINAL CONDITION
CaSiO ₃	CaAl ₂ Si ₂ O ₈	NaAlSiO ₄			
Primary Phase Pseudowollastonite					
60.0	20.0	20.0	30 min.	1,332°	Glass
			30	1,328	Glass and PWo*
40.0	20.0	40.0	45	1,197	Glass
			45	1,193	Glass and PWo
36.0	20.0	44.0	30	1,169	Glass
			30	1,165	Glass, PWo, and NE
50.0	40.0	10.0	30	1,287	Glass
			30	1,283	Glass and PWo
50.0	30.0	20.0	30	1,279	Glass
			30	1,275	Glass and PWo
50.0	20.0	30.0	30	1,275	Glass
			30	1,271	Glass and PWo
40.0	30.0	30.0	30	1,210	Glass
			30	1,206	Glass and PWo
37.0	15.0	48.0	30	1,174	Glass
			30	1,170	Glass, PWo, and NE
70.0	20.0	10.0	30	1,391	Glass and rare PWo
80.0	10.0	10.0	30	1,450	Glass
			30	1,441	Glass and rare PWo
40.0	10.0	50.0	30	1,185	Glass
			30	1,181	Glass and PWo
44.0	40.0	16.0	30	1,240	Glass
			30	1,236	Glass and PWo
37.0	33.0	30.0	30	1,192	Glass
			30	1,188	Glass and PWo
40.0	4.0	56.0	1 hr.	1,174	Glass
			1	1,170	Glass, PWo, and rare NE
36.0	28.0	36.0	30	1,184	Glass
			30	1,180	Glass and rare PWo
			30	1,176	Glass, PWo, and GEH
60.0	10.0	30.0	30	1,310	Glass
			30	1,306	Glass and PWo
Primary Phase Anorthite					
20.0	40.0	40.0	30 min.	1,249	Glass
			30	1,245	Glass and AN
40.0	40.0	20.0	30	1,249	Glass
			30	1,245	Glass and AN
10.0	60.0	30.0	30	1,395	Glass
			30	1,391	Glass and AN
30.0	60.0	10.0	30	1,399	Glass
			30	1,395	Glass and AN
10.0	18.0	72.0	30	1,458	Glass
			30	1,454	Glass and AN
30.0	40.0	30.0	30	1,245	Glass and rare AN
10.0	46.0	44.0	30	1,310	Glass
			30	1,306	Glass and AN
24.0	52.0	24.0	30	1,340	Glass and very rare AN
20.0	38.0	42.0	30	1,227	Glass and very rare AN

* PWo=pseudowollastonite, NE=nepheline, GEH=gehlenite (melilite), AN=anorthite, CG=carnegieite, $\beta\text{-AL}=\beta\text{-alumina}$.

TABLE 1—*Continued*

WEIGHT PER CENT			TIME	TEMP. (CENTIGRADE)	FINAL CONDITION
CaSiO ₃	CaAl ₂ Si ₂ O ₈	NaAlSiO ₄			

Primary Phase Anorthite— <i>Continued</i>					
35.0	35.0	30.0	30	I, 206	Glass
			30	I, 202	Glass, very rare AN
26.0	34.7	39.3	30	I, 199	Glass
			30	I, 195	Glass, AN, rarer NE
10.0	80.0	10.0	30	I, 510	Glass
			30	I, 502	Glass, very rare AN
44.0	46.0	10.0	30	I, 291	Glass
			30	I, 283	Glass, very rare AN
18.0	40.0	42.0	45	I, 257	Glass
			45	I, 253	Glass, very rare AN
31.0	45.0	24.0	30	I, 285	Glass
			30	I, 281	Glass and AN
30.0	34.0	36.0	30	I, 187	Glass
			30	I, 183	Glass and AN
			30	I, 174	Glass, AN, and GEH
3.0	55.0	42.0	30	I, 296	Glass
			30	I, 292	Glass and AN
			30	I, 288	Glass, AN, and rare β -AL

Primary Phase Nepheline					
20.0	20.0	60.0	1 hr.	I, 266	Glass
			45 min.	I, 262	Glass and NE
36.0	20.0	44.0	30	I, 169	Glass
			30	I, 165	Glass, NE, and PWO
30.0	30.0	40.0	1 hr.	I, 187	Glass
			I	I, 185	Glass, NE, GEH, β -AL
32.0	20.0	48.0	30 min.	I, 194	Glass
			30	I, 190	Glass and NE
20.0	36.0	44.0	1 hr.	I, 232	Glass
			I	I, 228	Glass and NE
20.0	30.0	50.0	30 min.	I, 250	Glass
			30	I, 246	Glass and NE
10.0	20.0	70.0	30	I, 327	Glass
			30	I, 323	Glass and rare NE
10.0	40.0	50.0	30	I, 284	Glass
			30	I, 282	Glass and NE
37.0	15.0	48.0	30	I, 174	Glass
			30	I, 170	Glass, NE, and PWO
38.0	10.0	52.0	90	I, 184	Glass
			90	I, 180	Glass, rare NE
25.0	30.0	45.0	30	I, 215	Glass
			30	I, 211	Glass and NE
30.0	25.0	45.0	30	I, 194	Glass
			30	I, 190	Glass and NE
20.0	25.0	55.0	30	I, 258	Glass
			30	I, 254	Glass, rare NE
22.0	15.0	63.0	30	I, 258	Glass
			30	I, 254	Glass and NE
3.0	35.0	62.0	30	I, 333	Glass, very rare NE

TABLE 1—*Continued*

WEIGHT PER CENT			TIME	TEMP. (CENTIGRADE)	FINAL CONDITION
CaSiO ₃	CaAl ₂ Si ₂ O ₈	NaAlSiO ₄			
Primary Phase Carnegieite					
16.0	10.0	74.0	30 min.	1,301	Glass
			30	1,298	Glass and CG
			30	1,293	Glass, CG, and NE
10.0	10.0	80.0	30	1,373	Glass
			30	1,369	Glass and CG
10.0	17.0	73.0	30	1,333	Glass
			30	1,329	Glass and CG
Primary Phase β-Alumina					
5.0	44.0	51.0	30 min.	1,296	Glass
			30	1,292	Glass and β-AL
			30	1,288	Glass, β-AL, NE, and AN
0.0	30.0	70.0	30	1,349	Glass
			30	1,245	Glass, β-AL, and NE
Primary Phase Gehlenite					
36.0	20.0	44.0	30 min.	1,170	Glass
			30	1,166	Glass, GEH, NE, and PWO
30.0	30.0	40.0	1 hr.	1,187	Glass
			1	1,183	Glass, NE, rare GEH
			2	1,174	Glass, GEH, NE
33.0	31.0	36.0	1	1,168	Glass
			1	1,166	Glass, rare GEH
			1	1,158	Glass, GEH, NE, and PWO
34.3	25.7	40.0	1	1,179	Glass
			1	1,175	Glass, very rare GEH

for many mixtures can be discussed only in terms of the parent-system, soda-lime-alumina-silica.

In Figure 7 the isotherms are omitted, only the fields of the primary phases being shown. Six fields have been outlined—in order of decreasing size, those of pseudowollastonite, anorthite, nepheline solid solutions, carnegieite solid solutions, β -alumina, and gehlenite (solid solutions). No wollastonite was encountered. This indicated that no substance enters into solid solution in the

wollastonite, to raise the inversion temperature appreciably.

In Figure 6 the nature of the surfaces of the fields can be ascertained from the isotherms. A solid model has been made and is shown in Figure 8. In the model the simple configuration of the field of β -alumina has been assumed. The surface for gehlenite (melilite) is rather flat but convex, the temperatures of the three apices of the triangular field being about $1,190^\circ$, $1,175^\circ$ and $1,169^\circ$ C.

The projections of the boundary curves

between the various fields are all essentially straight, except those between nepheline and carnegieite and between gehlenite and pseudowollastonite. The nature of the boundary curves is well shown in Figure 8; not so well shown is the maxi-

solid model along that boundary curve. The section is extended in the same direction across the field of gehlenite in order to exhibit temperature relations in that field.

The significance of the maximum must

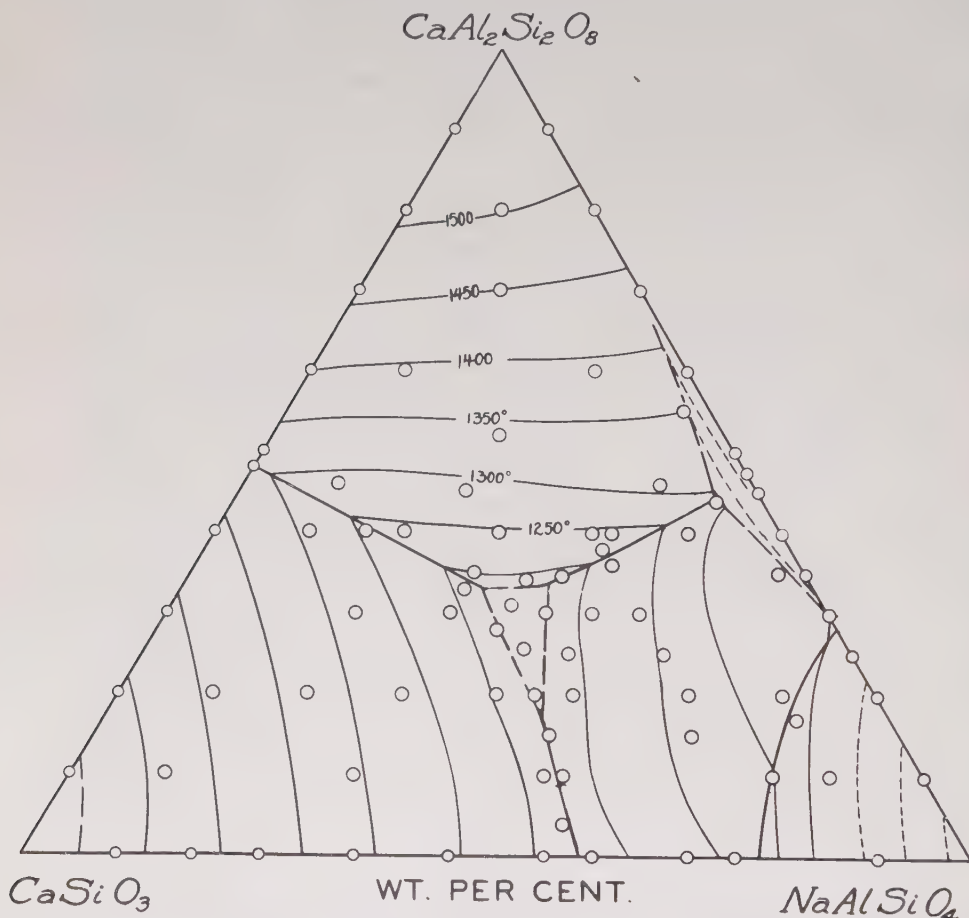


FIG. 6.—Phase relations in the system CaSiO_3 - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - NaAlSiO_4 , showing the various fields and the isotherms for 50° intervals. Location of mixtures given by circles, including those on the limiting systems determined by other workers.

imum on the boundary curve between pseudowollastonite and nepheline solid solutions, at about 10 per cent anorthite and a temperature of $1,180^\circ \pm 2^\circ \text{C}$. (see Fig. 7). The isotherms in Figure 6 indicate the presence of this maximum. In Figure 9 is presented a cross section of the

not be overlooked. Because of its presence and because there is reaction between pseudowollastonite and nepheline, liquids of a certain area in the composition triangle will become completely crystalline in the adjacent ternary system, CaSiO_3 - NaAlSiO_4 - Na_2SiO_3 , the ex-

tent of their travel into that system being determined in the usual manner by the position of three-phase triangles. For purposes of discussion of the paths of crystallization of liquids near the $\text{CaSiO}_3\text{--NaAlSiO}_4$ side of the system, the system

liquidus temperatures; there the upper part of the triangle is only outlined. The binary systems $\text{Na}_2\text{SiO}_3\text{--NaAlSiO}_4$ ²² and $\text{CaSiO}_3\text{--Na}_2\text{SiO}_3$ ²³ have been investigated. The field of carnegieite solid solutions has been indicated in full in Figure

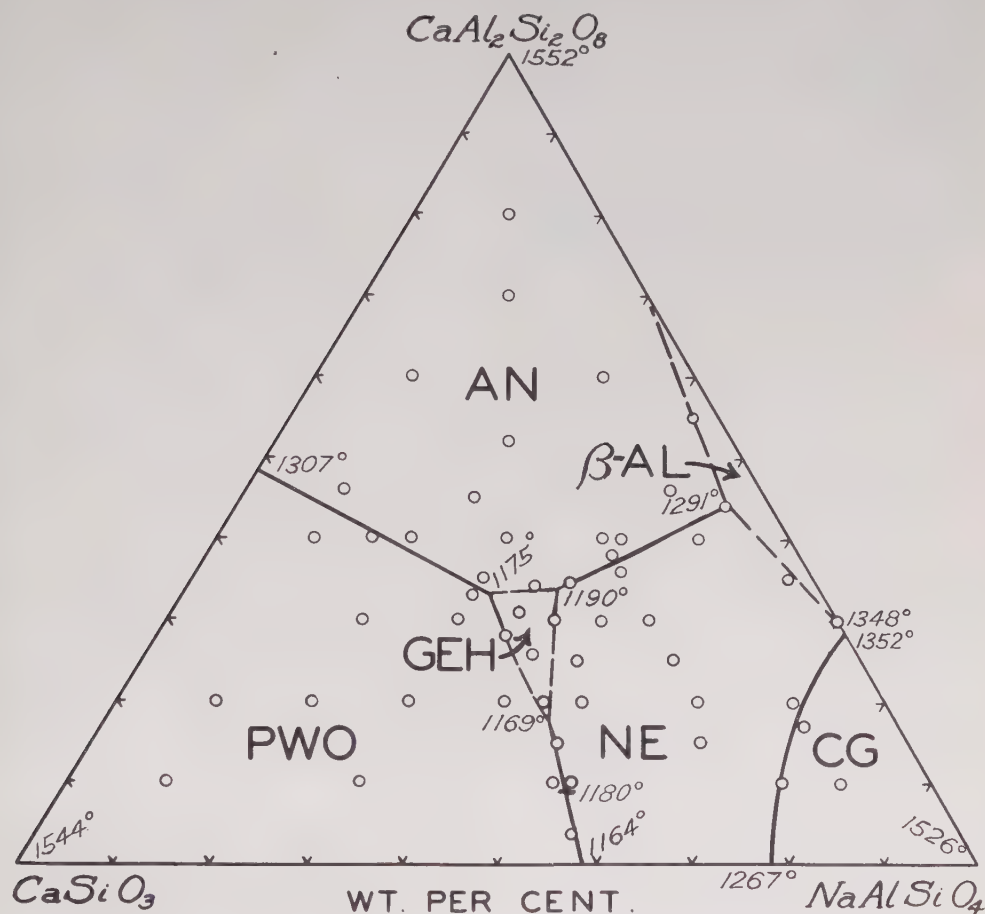


FIG. 7.—Phase relations in the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$, with isotherms omitted

$\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4\text{--Na}_2\text{SiO}_3$ must be considered. This system is shown in Figure 13. It is a plane section through the tetrahedron and has as its apices the compounds sillimanite (Al_2SiO_5), pseudowollastonite or wollastonite (CaSiO_3), and sodium metasilicate (Na_2SiO_3). Sillimanite does not form at

13 and merits considerable discussion at a later point.

The fields of gehlenite and beta-alumina.

—The field of β -alumina is small, a wedge

²² Tilley, *ftn.* 19 (1933).

²³ G. W. Morey and N. L. Bowen, "Melting Relations of the Soda-Lime-Silica Glasses," *Trans. Soc. Glass Tech.*, Vol. IX (1925), pp. 226-62.



FIG. 8.—The solid model

against the side $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$. It extends to a maximum of about 5 per cent CaSiO_3 . To picture crystallization in this field, we must visualize the position of the plane within the tetrahedron.

The fusion surface of gehlenite is of peculiar form. A cross section of that surface (Fig. 9) shows that it rises from its junction with the boundary curve between pseudowollastonite and nepheline and then falls to intersect the fusion surface of anorthite. In all, six mixtures were studied that lie either within the small triangular field or along its boundaries.

The extension of these extraneous fields across the plane of the present system will be more readily apprehended if we consider the relations in the system $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$. That system has been investigated by Rankin and Wright,²⁴ and the results of their study are presented in Figure 10. The system constitutes one face of the parent-tetrahedron. The join $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8$ lies on this face and is shown on the diagram

as AB. It can be seen that anorthite melts congruently but that a relatively small displacement of the boundary curve between anorthite and alumina would render anorthite unstable at its melting-point. Mentally adding the fourth component, Na_2O , to the system, we can picture the compound NaAlSiO_4 in its position on the face soda-alumina-silica. Now, within the tetrahedron there are boundary surfaces separating the various three-dimensional fields. Within the quaternary system the boundary surface between anorthite (plagioclase within the tetrahedron) and alumina intersects the join between anorthite and nepheline. Therefore, the phase alumina separates and occurs with the other two phases. The conditions determining just what modification of alumina is formed are not yet definitely understood, although it seems probable that " $\beta\text{-Al}_2\text{O}_3$ " is in reality a low-soda aluminate.

From the evidence obtained in the present study it is clear also that the field of gehlenite plunges toward and across the plane $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$; the V between the boundary curves *FC* and *CD* (Fig. 10)—meeting at the ternary eutectic between pseudowollastonite, anorthite, and gehlenite—be-

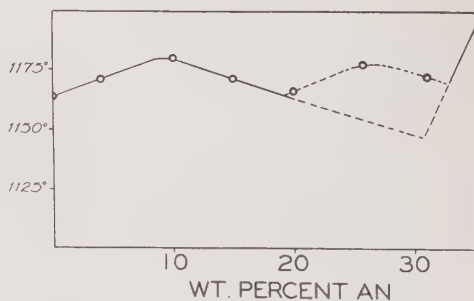


FIG. 9.—Cross section along the approximate plane of the boundary curve between pseudo-wollastonite and nepheline solid solutions and continuing through the field of gehlenite to the field of anorthite.

²⁴ Rankin and Wright, *ftn. 14* (1915).

comes a trough between two surfaces within the tetrahedron. That this trough does not penetrate to a great extent into the system under study is indicated by the fact that the gehlenite disappears by reaction at a temperature in the neighborhood of $1,150^\circ\text{C}$. At this tempera-

line. The movement of the point C toward the silica apex, or toward some point richer in soda and silica, indicates enrichment of liquids in those substances.

In runs on mixtures lying in the field of gehlenite some crystals were obtained

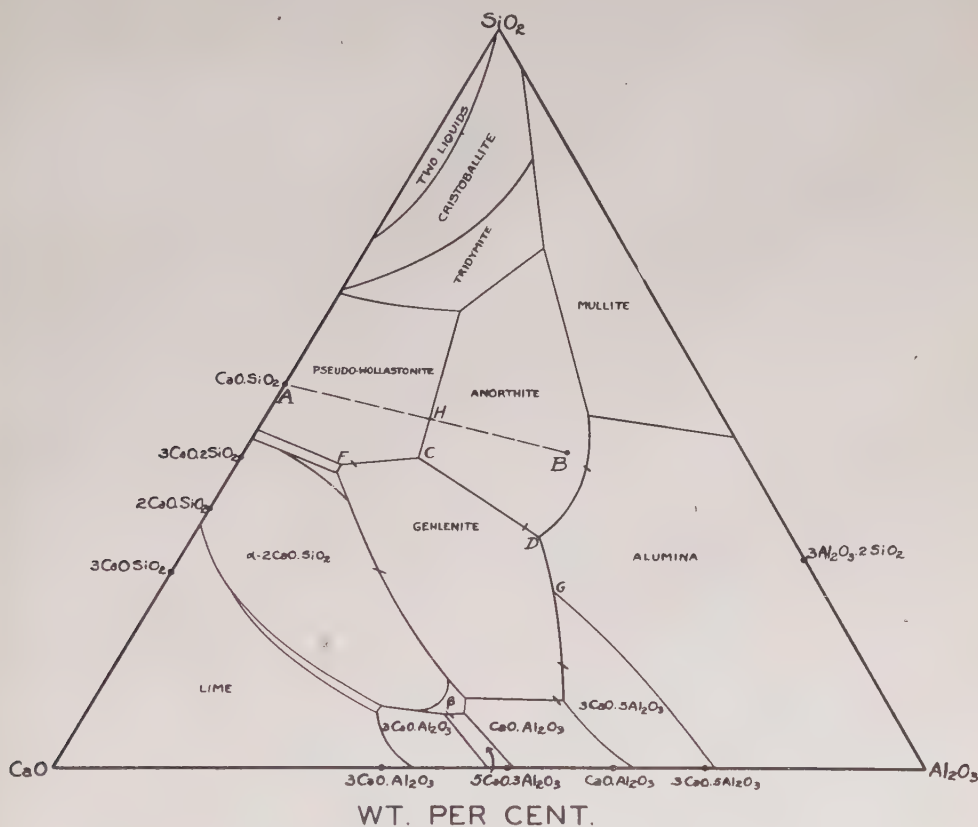


FIG. 10.—Phase relations in the system $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ (after Rankin and Wright)

ture within the tetrahedron there is a quaternary reaction point.

Thus it is demonstrated that within the quaternary system, at compositions near the center of the triangular plane representing the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$, the field of gehlenite (melilite) penetrates that plane. Similarly, the field of alumina has been pulled in to intersect the join anorthite-neph-

of which the properties were rather similar to those of β -alumina. However, the crystals were small and few, and positive identification was impossible. It was decided that they were probably gehlenite of markedly tabular habit, but the possibility that the field of alumina curves about sufficiently to penetrate the system in two areas is not altogether excluded.

Bowen²⁵ has found very similar relationships to those described above, as a result of the addition of NaAlSiO_4 to certain compounds of the system CaO-MgO-SiO_2 .²⁶ Bowen added nepheline to diopside and obtained akermanite, with sodic material in solid solution, along with forsterite, and a liquid which is enriched in " $\text{NaAlSi}_2\text{O}_6$." He concluded that nepheline desilicates the diopside, forming a melilite, which parallels the formation of gehlenite in the present nepheline mixtures. It is the opposite effect to that postulated by R. A. Daly,²⁷ who assumes desilication of the feldspathic molecules of magmas by lime, with the formation of feldspathoids.

EQUILIBRIUM CRYSTALLIZATION

Crystallization in the field of nepheline.—By virtue of the presence of the maximum M (Fig. 11), on the boundary curve between pseudowollastonite and nepheline solid solutions, liquids reaching that curve will thereafter move in a direction determined by their position with respect to that maximum. The three-phase triangles, XOP , XO^iP^i , and $XO^{ii}P^{ii}$ (Fig. 11), of which XOP is the limiting case, will move toward the "submerged eutectic" O ; triangles such as $XO^{iv}P^{iv}$, XO^vP^v , and so on, will move in the opposite direction. These two classes of three-phase triangles are separated by the straight line XMJ , and MJ is itself a three-phase boundary. The slope of the boundary curve is not sufficient to permit very accurate determinations of the three-phase boundaries. However, four such

boundaries were determined as accurately as possible, and the attitudes of the three-phase boundaries as presented are based on the results of those determinations. In Figure 11 the fields of gehlenite and β -alumina have been ignored for convenience in discussion.

Let us consider the crystallization of a liquid A (Fig. 11). On cooling to a temperature of about $1,275^\circ\text{C}$., nepheline solid solution containing less anorthite than P^{iii} separates. With continued cooling the liquid follows the curved path AO^{iii} , to the boundary curve, while the solid solution which separates becomes progressively richer in anorthite. When the liquid has just reached O^{iii} , the nepheline solid solution under equilibrium conditions has the composition P^{iii} . Pseudowollastonite now begins to separate, along with nepheline solid solutions, and the liquid moves along the boundary curve toward O . The nepheline solid solution becomes progressively richer in anorthite through reaction with the liquid. The last small amount of liquid is exhausted at O^{ii} , for now the base XP^{ii} of the three-phase triangle $XO^{ii}P^{ii}$ passes through the point of total composition, A . The final products of crystallization are pseudowollastonite and nepheline solid solution of composition P^{ii} . Even if gehlenite were formed, that phase must disappear eventually and would not be present in the final products. Such behavior is typical of liquids lying to the "north" of the join XMJ . Ignoring gehlenite, only those liquids lying to the "north" of the base XP of the triangle XOP will yield anorthite among the products of crystallization.

A liquid of composition B begins to crystallize with the separation of a nepheline solid solution poorer in anorthite than P^{iv} . The liquid will follow the

²⁵ "Genetic Features of Alnoitic Rocks at Isle Cadieux, Que.," *Amer. Jour. Sci.*, Vol. III (5th ser., 1922), pp. 1-34.

²⁶ J. B. Ferguson and H. E. Merwin, "The Ternary System, CaO-MgO-SiO_2 ," *Amer. Jour. Sci.*, Vol. XLVIII (4th ser., 1919), pp. 81-123.

²⁷ *Igneous Rocks and the Depths of the Earth* (New York: McGraw-Hill Book Co., 1933).

curved path BO'' , while the nepheline becomes richer in anorthite until, when the liquid has the composition O^{iv} , the nepheline is P^{iv} . Pseudowollastonite will now begin to separate also, and the liquid will move toward O^{vi} . The nepheline solid solution becomes progressively poorer in anorthite. The liquid is exhausted at O^v when the base XP^v of the

a three-phase triangle of which the liquid apex lies at O^{vi} will be completely crystallized at O^{vi} . For those liquids the final nepheline solid solutions will have the composition P^{vi} (actually about $\text{Ne}_{92}\text{--An}_8$). Liquids lying to the "south" of the base of that three-phase triangle will be completely crystallized at points along the curve $O^{vi}S$, within the system Ca -

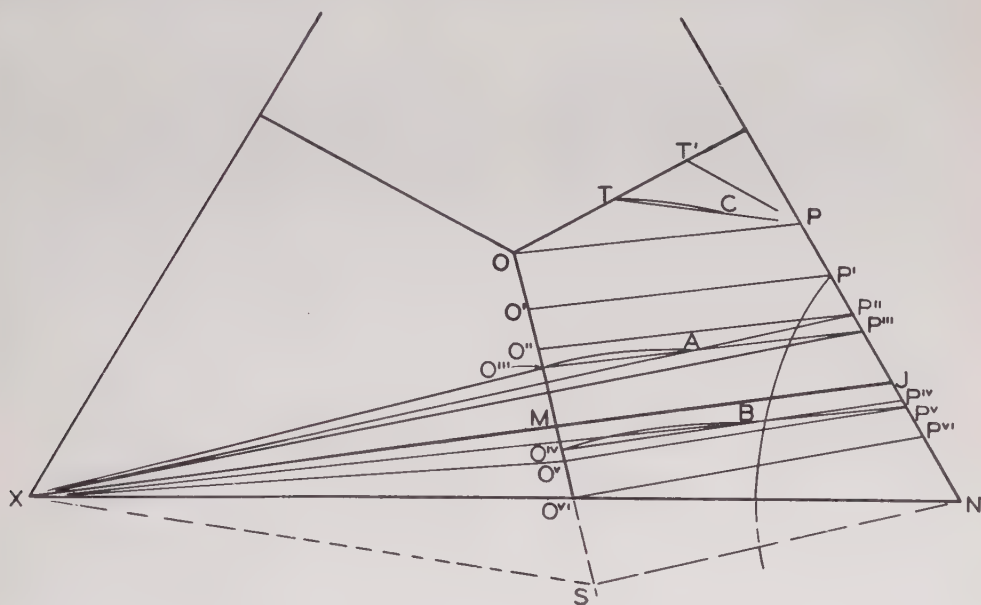


FIG. 11.—Crystallization in the field of nepheline

triangle XO^vP^v passes through B . The products of crystallization will be pseudowollastonite and nepheline solid solution of composition P^v . It should be noted that during the crystallization of a liquid lying "south" of the join XMJ , while the liquid moves across the field of nepheline, the solid solution which separates becomes continuously richer in anorthite. But, when the liquid moves from O^{iv} to O^v , the solid solution is made over to varieties progressively poorer in anorthite. The effect is perhaps not large, but it is real.

Those liquids lying on the base XP^{vi} of

$\text{SiO}_3\text{--NaAlSiO}_4\text{--Na}_2\text{SiO}_3$. The farther a liquid moves into that system the poorer in anorthite is the nepheline solid solution that is produced, although there is a limit to this process. It is unlikely that pure nepheline will ever be formed under conditions of equilibrium, since CaSiO_3 is always present in the liquids and therefore $\text{CaAl}_2\text{Si}_2\text{O}_8$ is developed.

Even under conditions of equilibrium, then, liquids of composition lying in a certain area of the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ move into the adjacent system. In Figure 11 the point S has been suggested as the limit of move-

ment of those liquids. However, it is very unlikely that true relations can be shown in so simple a fashion; it is possible that certain liquids will actually reach a reaction point in the system $\text{CaSiO}_3\text{--NaAlSiO}_4\text{--Na}_2\text{SiO}_3$.

It will be noted that the three-phase boundaries TP and T^iP in Figure 11 have been constructed on the assumption that the composition of the most concentrated solid solution of anorthite in nepheline remains constant with falling temperature. As suggested previously, that relation is not established with certainty, but it is here assumed to be true for simplicity. A liquid of composition C will begin to crystallize with the separation of nepheline solid solution containing less anorthite than P ; and, when the liquid has moved along the curve CT to T , the nepheline solid solution has the composition $P(\text{Ne}_{65}\text{An}_{35})$. Now, anorthite begins to separate from the liquid, which moves along the boundary curve toward O . All such liquids will reach O and will yield as the final products of crystallization nepheline solid solution (P), anorthite, and pseudowollastonite. Gehlenite will be formed at some stage but will disappear eventually under equilibrium conditions.

Crystallization in the field of carnegieite.—Crystallization is still more complicated for mixtures in the field of carnegieite. According to Bowen,²⁸ carnegieite takes up to 5 per cent anorthite in solid solution. Therefore there will be a set of three-phase boundaries in the carnegieite field (GK , G^iK^i , etc., Fig. 14). By virtue of the behavior of certain liquids the relations in the adjacent ternary system must be considered. Tilley²⁹ has investigated the system $\text{Na}_2\text{SiO}_3\text{--NaAlSiO}_4$, and for completeness his

results are presented in Figure 12. This system is unusual in that it is the high-temperature form of one of the components that forms solid solutions, in consequence of which the temperature of inversion of carnegieite to nepheline is lowered to $1,163^\circ\text{C}$. Liquids containing up to 23 per cent Na_2SiO_3 will, upon cooling, yield carnegieite solid solutions which become continuously richer in Na_2SiO_3 as the temperature falls. Eventually the liquid is exhausted and carnegieite solid solution alone remains, and this will cool as such through a narrow range of temperature. Then the carnegieite begins to invert to nepheline, and the inversion continues in the solid state until the temperature falls to $1,163^\circ\text{C}$. At that temperature liquid forms again, and the temperature remains constant until all the remaining carnegieite solid solution has inverted and the mixture consists of nepheline and liquid. With further cooling the amount of nepheline increases and the liquid decreases, until at 908°C . sodium metasilicate also separates and the liquid is exhausted at that temperature. The important point lies in the fact that here carnegieite solid solutions but no nepheline solid solutions are formed; whereas in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ the nepheline solid solutions are very important and the carnegieite solid solutions minor and, it must be admitted, not exactly determined. There will be, then, a field of carnegieite solid solutions of ternary nature, common to the two systems being discussed. One particular carnegieite solid solution has a composition that can be expressed as about 95 per cent NaAlSiO_4 and 5 per cent CaSiO_3 (see Fig. 13).

In Figure 14 that area of ternary solid solutions is indicated on a diagram, which, it must be stressed, is considerably distorted to facilitate discussion.

²⁸ Bowen, *ftn.* 7 (1912).

²⁹ Tilley, *ftn.* 19 (1933).

The three-phase boundaries of the *GK* type join liquids on the boundary curve between nepheline and carnegieite solid solutions with the appropriate carnegieite solid solutions along the line bounding the area of those ternary solid solutions. Besides those lines, there is another set joining liquids on the same boundary

limiting one in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$ is available from Figure 4. Besides these two sets of tie-lines, we must consider the three-phase boundaries of the *OP* type.

A liquid of the composition *A* (Fig. 14) begins to crystallize with the separation of a carnegieite solid solution whose

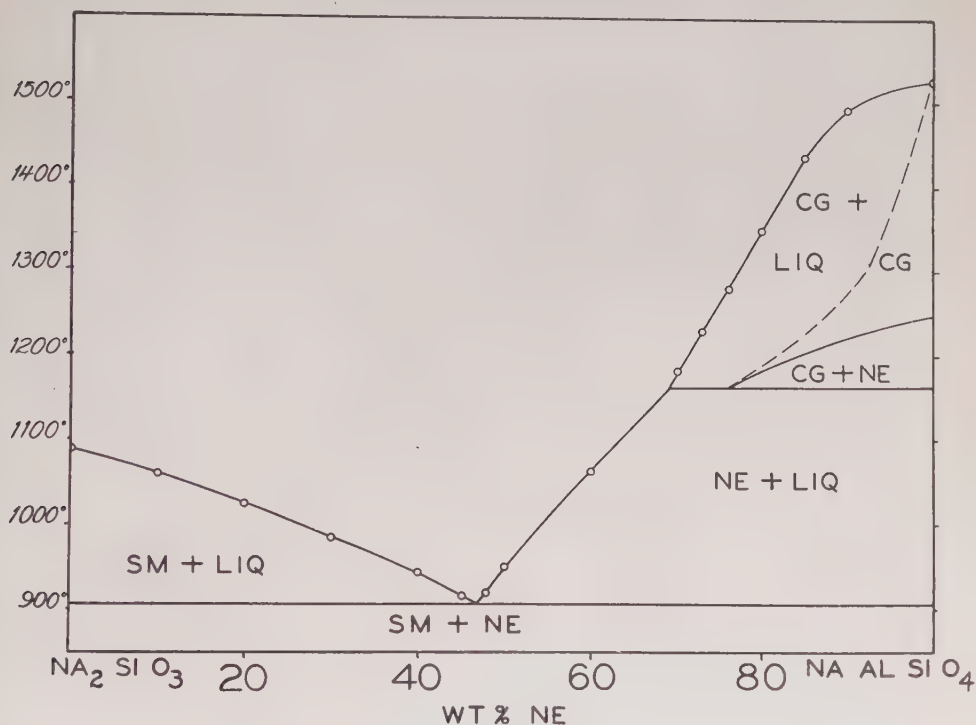


FIG. 12.—Phase relations in the system $\text{Na}_2\text{SiO}_3\text{--NaAlSiO}_4$ (after Tilley)

curve with the nepheline solid solutions with which they are individually in equilibrium; those lines are shown by *GH*, *GⁱHⁱ*, and so forth, and will be termed the *GH* type of three-phase boundary. If the carnegieite solid solutions, and also the nepheline solid solutions, were binary in nature, then that second set of tie-lines could be obtained from Bowen's diagram (see Fig. 4). However, since that is not true, the tie-lines are only approximately located. The

composition lies in the area of ternary solid solution on the tangent to the curve of crystallization at *A*. It will be poorer in anorthite than *K*. With continued cooling the solid solution becomes richer in anorthite, and the liquid follows the curved path *AG*. At the point *G*, when the carnegieite has the composition *K*, it begins to invert to nepheline solid solution *H*. As the temperature falls, the liquid changes in composition along the boundary curve to *Gⁱ*,

the carnegieite continuously inverting to nepheline solid solutions which attain the composition of H^i when the liquid reaches G^i . At G^i the last trace of carnegieite has the composition K^i . The point of total composition, A , lies on a three-phase boundary of the OP type,

through the point A ; and the final products of crystallization are pseudowollastonite and nepheline solid solution containing slightly more anorthite than P^i .

A liquid of composition B behaves in a fashion similar to that described above,

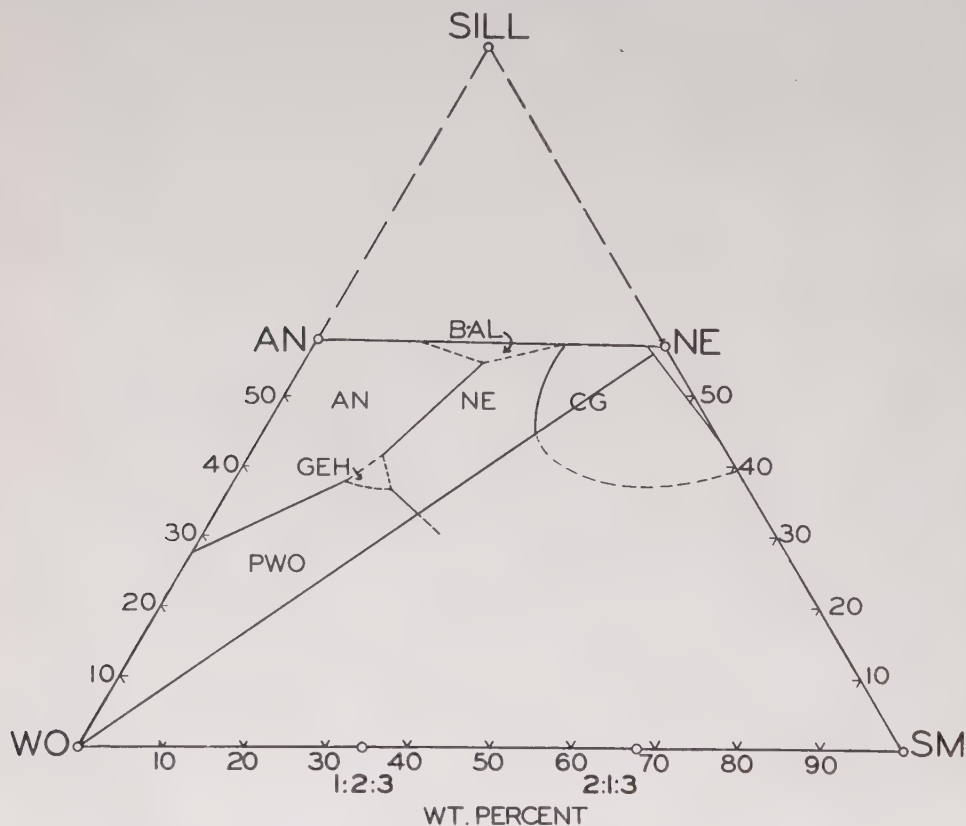


FIG. 13.—The section through the tetrahedron (see Fig. 1). Showing phase relations in the system investigated and the field of carnegieite ternary solid solutions.

namely, O^iP^i . Therefore the liquid must reach the boundary curve between pseudowollastonite and nepheline at O^i . To do so, it follows the curved path G^iO^i , while crystals of nepheline solid solution separate which are continuously richer in anorthite. At O^i the nepheline has the composition P^i . The liquid is exhausted a short distance "north" of O^i , when the base of a three-phase triangle passes

but there are two points of interest. First, not only does the liquid travel a considerable distance along the boundary curve between the fields of nepheline and carnegieite, but it crosses the join MJ twice. Since the original composition lies "south" of MJ , the liquid must return to this side. Second, while the liquid goes from G^i to G^{ii} , the nepheline solid solution increases in amount but becomes

progressively poorer in anorthite. Then, while the liquid changes in composition along the curve $G^{ii}O^{ii}$, the nepheline solid solution which separates becomes richer in anorthite, for, when pseudowollastonite begins to separate, the nepheline solid solution has the composition

P^{ii} . Now, however, further cooling results in the opposite effect, namely, the nepheline solid solution becomes poorer in anorthite again, and the final solid solution contains slightly less anorthite than P^{ii} .

The crystallization of a liquid C is

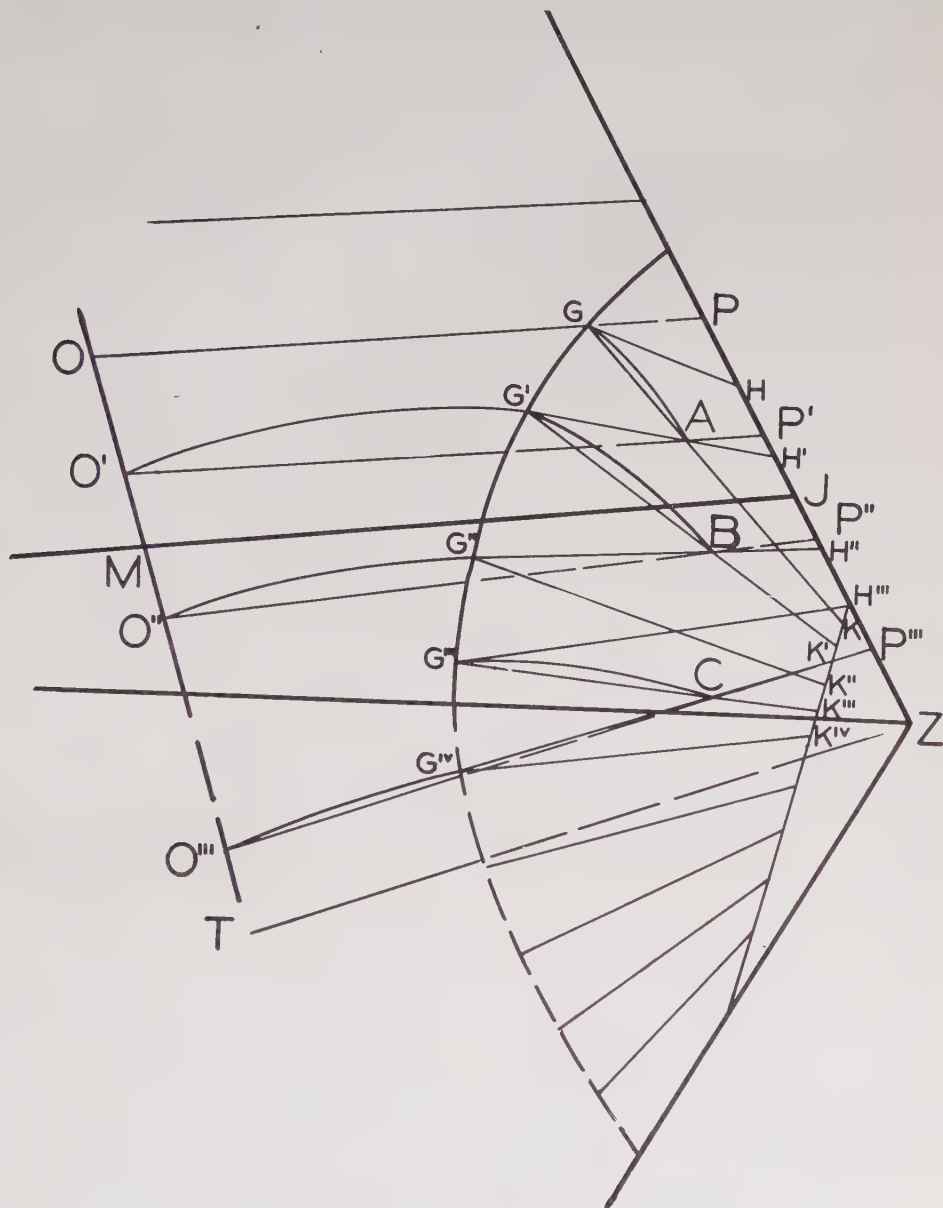


FIG. 14.—Crystallization in the fields of carnegieite and nepheline

again similar, but this liquid becomes completely crystalline somewhere below O''' in the adjacent system.

Crystallization of liquids in other fields.

—In Figure 15 are represented the lines that determine courses of crystallization in the system, omitting the complications

Figure 15 that complexity is ignored; courses of crystallization radiate from the anorthite apex. The small amount of solid solution of nepheline in anorthite is neglected.

For liquids which yield nepheline solid solution as the secondary phase the re-

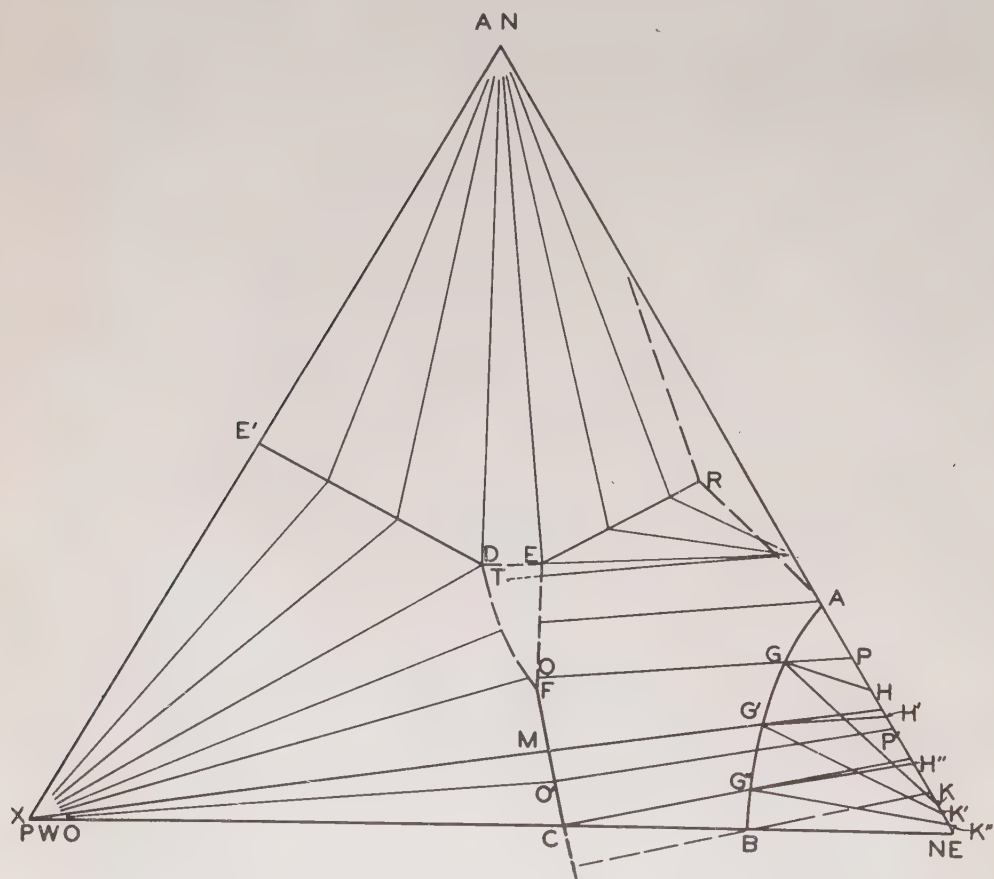


FIG. 15.—Showing generalized tie-lines in the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$

just described. The behavior of all liquids in the field of pseudowollastonite is presumably ternary and therefore is simple. It has already been mentioned that the phase separating from liquids in the field of anorthite is not anorthite but is, rather, a basic plagioclase. In

lations between liquid and solid solutions are determined by three-phase triangles in the manner discussed above.

Mixtures whose compositions lie in the fields of β -alumina or gehlenite behave initially in a manner which requires consideration of the four-component system.

With equilibrium crystallization no β -alumina or gehlenite will be present in the final products.

SIGNIFICANCE OF VARIOUS NEPHELINE SOLID SOLUTIONS

The indices of pure artificial nepheline are $\omega = 1.537$ and $\epsilon = 1.533$; those of the

of composition C (23 per cent An). C represents the composition of that nepheline solid solution which is isotropic. The join AB represents the approximate locus of liquids from which separate isotropic nepheline solid solutions as the primary phase. The dashed line BC is a three-phase boundary; that is, the liquid

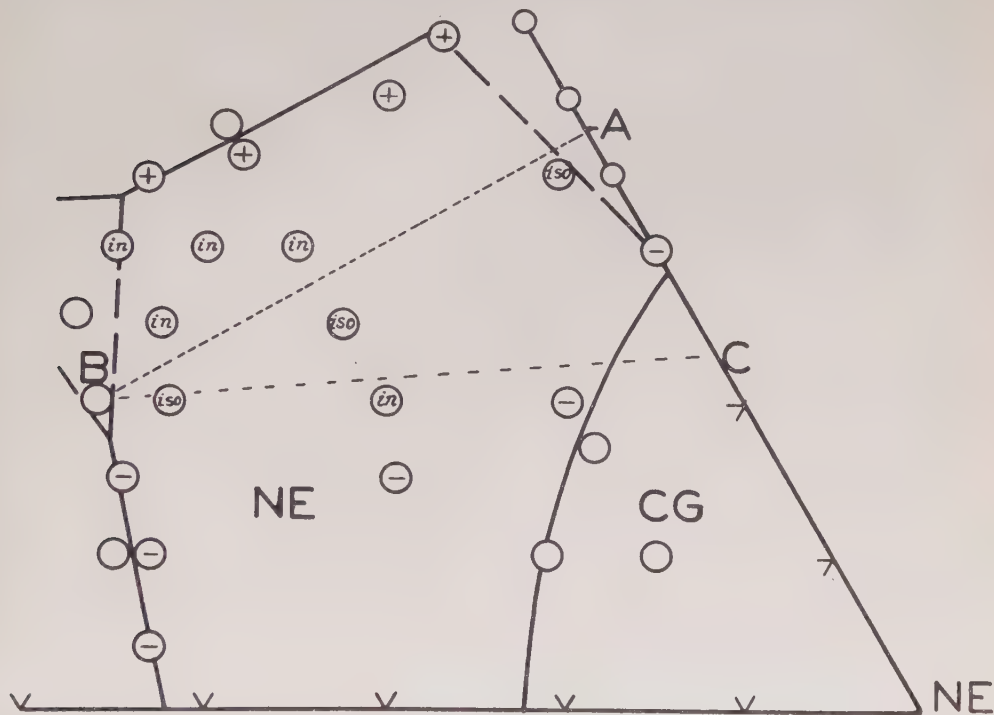


FIG. 16.—Showing the variation in the sign of the nepheline solid solutions obtained as primary phases in liquids of different compositions in the field of nepheline. $\oplus$ = positive; $\ominus$ = negative; *iso* = isotropic or nearly so; *in* = indeterminate.

limiting solid solution, $\text{Ne}_{65}\text{An}_{35}$, are $\omega = 1.537$ and $\epsilon = 1.539$. No accurate determinations of the indices of the nepheline solid solutions have been made in this study, but the sign of the nephelines obtained at liquidus temperatures in various mixtures has been plotted on the composition triangle.

The liquid A (37.5 per cent An) is in equilibrium with nepheline solid solution

B is in equilibrium with nepheline solid solution of composition C .

Unfortunately, the crystals obtained in runs at or near liquidus temperatures were so small that in several examples their optical properties were not determinate. At best, there is outlined a zone in which isotropic or nearly isotropic nepheline solid solutions are the primary phase, but in compositions out-

side this zone the optical character was usually definite.

FRACTIONAL CRYSTALLIZATION

The results of fractional crystallization of liquids in the system CaSiO_3 – $\text{CaAl}_2\text{Si}_2\text{O}_8$ – NaAlSiO_4 may be briefly outlined (see Fig. 17). All those liquids which reach the “eutectic” will yield, as the final products of fractional crystal-

CaSiO_3 – NaAlSiO_4 – Na_2SiO_3 ; with fractionation they will move farther into that system than will liquids under equilibrium conditions. The final liquid is enriched in sodium metasilicate, and that substance may possibly be present in the products of crystallization.

Therefore, liquids which move initially in opposite directions nevertheless become more alkaline eventually. It is of

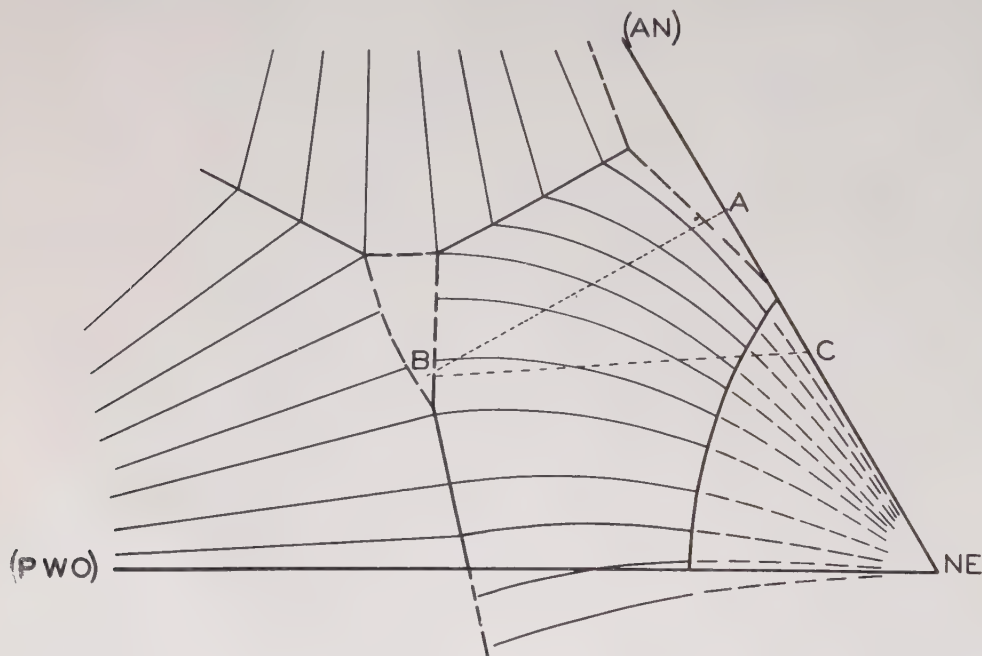


FIG. 17.—Paths of fractional crystallization in part of the system CaSiO_3 – $\text{CaAl}_2\text{Si}_2\text{O}_8$ – NaAlSiO_4

lization, pseudowollastonite, anorthite (actually plagioclase), nepheline solid solutions, and gehlenite. From some liquids β -alumina will also separate and will remain if reaction is prevented. The formation of gehlenite or β -alumina causes the liquid to become enriched in albite. If in some manner the gehlenite and β -alumina are prevented from reacting with the liquid, the residual liquid may be relatively rich in albite and yield sodic plagioclases.

Some liquids will enter the system

interest to note that two liquids whose compositions are almost identical but one of which lies just “north” and the other just “south” of the maximum will yield, with fractionation, products having quite different constitutions. That liquid to the “north” of *M* will yield gehlenite, nepheline solid solution, plagioclase, and pseudowollastonite. That to the “south” will yield pseudowollastonite, nepheline solid solutions, double metasilicates, and Na_2SiO_3 .

The joins *AB* and *BC* in Figure 17

have been transferred from Figure 16. A tangent to any curve of fractional crystallization at the point where that curve cuts the line AB will pass through the point C , the composition of the isotropic nepheline solid solutions. From consideration of the fractionation curves it may be seen that, if zoned nephelines are formed, they may possess cores of negative optical character, intermediate zones of isotropic material, and outer mantles of positive character.

PETROLOGIC SIGNIFICANCE

THE SODA-LIME-ALUMINA-SILICA SYSTEM

The oxides Na_2O , CaO , Al_2O_3 , and SiO_2 that form the parent-tetrahedron are of prime importance in petrology. Together they comprise 90 per cent by weight of the average of 546 granites, 85 per cent of the average of 43 nepheline syenites, and 77 per cent of the average of 161 basalts.³⁰ The present study is but a small fraction of the wealth of data now amassed on this and other systems and, with the increasing incorporation into such studies of other variables, such as pressure and volatiles, may need to be reconsidered as to its practical bearing. However, several interesting observations may be made.

THE WOLLASTONITE-ANORTHITE-NEPHELINE SYSTEM

There are no natural magmas showing close approach to liquids of the system except anorthosites. The "submerged eutectic" has a composition rather similar to the average of twelve anorthosites as given by Daly, but that rock type has a considerably different mineral constitution. The present system exhibits no striking differences in size of the fields of primary phases; therefore it yields no

corroboratory evidence as to the order of crystallization in magmas. It is known that the three chief natural mineral equivalents—wollastonite, plagioclase, and nepheline—may crystallize both early and late.

However, there is a definite similarity between the products of fractional crystallization of some liquids within the system and minerals in alkaline rocks in nature. One can obtain from these mixtures pseudowollastonite, gehlenite, nepheline solid solution, and plagioclase, an assemblage which is comparable with the mineral content of such rocks as nepheline tephrite, nepheline basalt, and types of theralites, with nepheline, melilite, augite, or alkaline pyroxene, and usually basic plagioclases.

The significance of the field of gehlenite.—Daly³¹ and Tilley and Harwood³² have stated that melilite, at least in some instances, has formed in certain rocks as a result of the contamination of a magma by assimilation of limestone. They believe that excess CaO derived from limestone unites, for example, with diopside to yield akermanite or with anorthite to yield gehlenite (and wollastonite). The formation of the gehlenite in the present instance is apparently the result of desilicating action by nepheline on the lime-rich silicates, a reaction very similar to that postulated by Bowen³³ to explain the formation of melilite from augite by the action of residual alkaline liquid in alnoitic rocks. The nepheline, whose affinity for silica is well known, presumably becomes albite (or analcite) through that reaction, and that compound may then enter into both anor-

³¹ *Ibid.*

³² Ftn. 1 (1931).

³³ Ftn. 25 (1922).

³⁰ Daly, ftn. 27 (1933).

thite and nepheline³⁴ in solid solution. Tilley and Harwood believe that in the Scawt Hill rocks silica was taken from albite by lime derived from wall rocks, with resultant formation of wollastonite and nepheline principally.

Thus, there are two possible actions which are diametrically opposed, but both may occur in nature; it is improbable that one process will occur to the exclusion of the other.

The significance of the field of alumina.—Until recently it was believed that anorthite, as a relatively pure compound, could form in melts with nepheline; however, the work of Schairer has demonstrated that free alumina crystallizes from such melts over a certain composition range and that, as a consequence, plagioclase rather than anorthite is formed. The results of the present study are in agreement with those facts. This effect, thus experimentally shown, may explain to some extent the presence of corundum in nepheline-plagioclase-bearing rocks, which are a natural habitat of corundum. J. S. Shand³⁵ is very insistent that the corundum-bearing nepheline rocks, occurring particularly as pegmatites, are the result of contamination of a parent-granitic or syenitic magma by lime-rich rocks. In this opinion Shand agrees essentially with Daly, who believes the parent-magma may range from basaltic to granitic.

In the corundum-bearing syenitic rocks the plagioclase is commonly a sodic variety; in synthetic mixtures the field of alumina does not penetrate the system albite-nepheline. But it may well be that the addition of K_2O , MgO , and

the other substances of natural magmas causes a further expansion of the field of alumina in the multicomponent system, so that the same reaction effect is present between albitic plagioclases and nepheline.

Corundum occurs, however, not only in the rock types just discussed but also in types with basic plagioclases. W. G. Miller³⁶ has reported the occurrence of a corundum-gabbro which is associated apparently with the nepheline rocks of Ontario. Plagioclase and hornblende are the only other constituents. The occurrence of corundum in basic alkaline rocks has been described by many others. Therefore, the development of free alumina by reaction between nepheline and basic plagioclase may well be a clue to the formation of corundum in some natural magmas.

The "plagioclase effect."—Of interest not only from the petrologic but also from the experimental viewpoint is the fact that, when lime is present in mixtures containing the albite molecule, some anorthite is produced by reaction, and consequently a plagioclase. This effect has been noted by Schairer and Bowen³⁷ and by others. The work of Foster also suggested that, when lime is added to mixtures containing nepheline, anorthite is formed, and this has been verified in the present study.

Similarly, when soda—for example, in nepheline—is added to anorthite-bearing mixtures, the albite molecule is formed, and therefore plagioclase is again produced. Consequently, it is unlikely that the pure end-members of the plagioclase

³⁴ Greig and Barth, *ftn. 10* (1938).

³⁵ *Eruptive Rocks* (London: Thos. Murby & Co. 1927).

³⁶ "Notes on the Corundum-bearing Rocks of Eastern Ontario," *Amer. Geol.*, Vol. XXIV (1899), pp. 276–82.

³⁷ Unpublished data.

series can form in any mixture containing both soda and lime. It is not surprising that in natural igneous rocks the pure compounds are never found.

Final-stage soda-rich liquids.—It has been shown that, even under equilibrium conditions, liquids of a certain composition range become enriched in sodium metasilicate; that is, they leave the system $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$. For those liquids fractional crystallization accentuates that effect. It is often stated in the literature that the final-stage solutions of consolidating magmas are rich in soda and silica and that the common formation of albite in great amount as a mineral late in the history of crystallization of igneous rocks is due to the action of those liquids.³⁸ It is very likely that the production of final liquids rich in soda and silica, in the mixtures of the present study, has some bearing on the natural process of albitization. Other systems have been studied in which final liquids of the same general character may be developed.

Possible significance of the maximum.—It is clear that two liquids, whose compositions are almost identical but one of which lies "north" and the other "south" of the maximum (M , Fig. 11), will move in opposite directions under any conditions of crystallization. The one liquid may yield gehlenite, pseudowollastonite, anorthite, and nepheline solid solutions; whereas the other may yield pseudowollastonite and nepheline solid solutions of quite different character, and perhaps also sodium metasilicate. If a natural

magma were such that its position in a multicomponent system lay very near such a critical composition and if some process changed that composition even very little in the appropriate direction, it can be understood how the modified liquid might follow a path of crystallization quite different from that followed by the unmodified magma.

Among the possible factors that might cause such a change in the composition of a magma, the following may be mentioned. Assimilation is believed by many to be an all-important factor in the production of rock varieties. Other students are inclined to believe that assimilation is a minor process. But only a small amount might in special cases be sufficient to change the composition of a magma so as to result in different products of crystallization. The course of crystallization may also be changed by absorption of material through reaction with the magma. Again, if a certain reaction that normally takes place fails to do so for any reason, a magma may yield products different from those it ordinarily develops.

Zoned nephelines.—Nephelines with zones of considerable variation of composition and of which the optical characteristics vary considerably may result from the fractional crystallization of liquids whose compositions lie in the fields of nepheline or carnegieite. It does not seem improbable that these relationships obtain in natural magmas. In fact, zoned nephelines have been described by several workers, and Shand³⁹ has recently summarized a few occurrences with particular reference to the alkaline

³⁸ R. J. Colony, "The Final Consolidation Phenomena in the Crystallization of Igneous Rocks," *Jour. Geol.*, Vol. XXXI (1923), pp. 169-78; G. H. Anderson, "Granitization, Albitization and Related Phenomena in the Northern Inyo Range of California-Nevada," *Bull. Geol. Soc. Amer.*, Vol. XLVIII (1937), pp. 1-74.

³⁹ "On the Staining of Feldspathoids, and on Zonal Structure in Nepheline," *Amer. Min.*, Vol. XXIV (1939), pp. 508-13.

lavas of the African Rifts. He mentions a variation in refringence and birefringence in the various zones. Truly isotropic nephelines are not found in nature; no nepheline contains that much anorthite. But many crystals exhibit a core of normal refraction and birefringence, followed by a narrow zone of weaker refraction and birefringence, and outside that a narrow zone of higher refraction but weak birefringence. Such zoning has been explained as due to rhythmic variation in the anorthite content of the solid solu-

tions; but the zones observed by Shand were due to variation in other nepheline components, for the most part.

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